THE DEGRADATION OF AZINPHOSMETHYL APPLIED TO TRELLISED APPLES

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ABSTRACT

During May through July, 1988, a degradation study of dislodgeable azinphosmethyl (Guthion^{R}) residues on apple foliage in two orchards was conducted in Madera County. The trees were trellised and were watered by an overhead sprinkler system which delivered 3.6 inches of water per week. The California Department of Food and Agriculture (CDFA) and the cooperating grower were interested in characterizing the dissipation of azinphosmethyl under these conditions. To better describe the pattern of dissipation, the foliage was sampled at three heights in the canopy. The data were also employed to estimate decay rates at each height. Each orchard was divided into four distinct plots. Within each plot, three samples were taken. Each sample consisted of 40 leaf discs from one height interval. Samples were collected at varying intervals from one day pre-application to 56 days post-application and analyzed for azinphosmethyl and azinphosmethyl oxon residues. Azinphosmethyl oxon (range: 0.002-0.011 ug/cm^2) was detected in one-third of the samples and constituted about one to five percent of the thion levels. Study results showed that there was a significant difference in initial deposition by height. Although the decay rates at four, seven and 11 feet were slightly different, the rates did not appear to be related to the height in the canopy.

INTRODUCTION

This study was conducted to determine and characterize initial deposition and decay rates of azinphosmethyl on apple foliage. Azinphosmethyl (O,O-dimethyl S-[4-oxo-1,2,3-benzotriazin-3(4H)-yl) methyl] phosphorodithioate is a toxicity category one insecticide used for the control of many insect pests in a wide variety of fruit, vegetable, nut, melon and field crops as well as ornamentals, fruit and shade trees. It has an oral LD_{50} of 11 mg/kg and a dermal LD_{50} of 220 mg/kg in the female rat (2). Azinphosmethyl is typically applied to apples up to three times per year to control coddling moth.

MATERIALS AND METHODS

With the assistance of the Madera County Agricultural Commissioner and the cooperating grower, two apple orchards were selected and monitored for two to eight weeks. The apple trees were trellised in rows, with 174 trees per row and 726 trees per acre. The canopy was 10-14 feet high, with an eight foot planting distance between trees and the rows spaced 14 feet apart.

The variety was Granny Smith. The trees were irrigated by an overhead sprinkler system which delivered 3.6 inches of water per acre each week over the course of the study.

Guthion^{R} 35 percent WP (Mobay) was applied to the south orchard 10 days before sampling began at the rate of 3 pounds per acre (1.05 lb active ingredient (a.i.)/acre) in 50 gallons of water. Guthion^{R} 35 percent WP was applied to the north orchard at the rate of 1.75 pounds per acre (0.61 lb a.i./acre), in 30 gallons of water. Analysis of a tank mix sample from this application confirmed this rate, showing azinphosmethyl present at a concentration equivalent to 0.62 lb a.i./ acre. A Windmill electrostatic sprayer was used for all applications. For both orchards, the overhead irrigation began the day after application. The south orchard had been irrigated once (3.6" in 7 days) prior to the first sampling interval. No worker activity took place in either orchard during the course of this study.

The orchards were evaluated using a sampling strategy adapted from the methods of Iwata, et al. (4), according to the following scheme: Four plots were selected from each orchard and one row selected from each plot as the sampling area; the rows were marked with flagging tape. Within the row, four areas, two on each row side, were marked with flagging tape. Ten foliage discs were collected from each area at each of three heights: 4 feet, 7 feet and 11 feet, for a total of 40 leaf discs (per sample) per plot at each height interval.

The leaf discs were collected using a Birkestrand leaf punch, 2.5 centimeters in diameter, fitted with a four ounce jar. Each jar was then sealed with aluminum foil, capped and stored immediately on ice. Samples were shipped to CDFA Chemistry Laboratory Services in Sacramento for extraction within 24 hours.

The south orchard was sampled at 8 and 14 days post-application. The north orchard was sampled one day before application and at 1, 2, 5, 8, 14 and 28 days post-application for all heights. In addition, the 7-foot height was sampled at 42, 49 and 56 days post-application and the 4-foot height at 56 days post-application. Each foliage sample was analyzed by the CDFA Chemistry Laboratory for dislodgeable residues of azinphosmethyl and azinphosmethyl oxon. Residues were rinsed from the leaf surface using a water-surfactant solution, then extracted from the aqueous solution with ethyl acetate. Analysis was by gas chromatography. The limit of detection for azinphosmethyl was 0.002 ug/cm^2 and, for the oxon, 0.003 ug/cm^2.

The residue data were transformed by taking the logarithms and a conventional least squares linear regression analysis was done on the transformed residue data versus the day post-application. A half-life estimate was then derived using the first order rate constant obtained from the linear regression analysis. The first-order exponential decay model takes the following form (5,6,7):

$$Y = A + B * \log_{10}(R)$$

where A = initial deposition in ug/cm^2
B = first order rate constant in (ug/cm^2)/time in days
and R = mean residue at each sampling interval in ug/cm^2

The equation for estimating the half-life of the residues is as follows:

$$t_{1/2} = [\log_{10}(1/2)]/B$$

where t = estimated half-life in days
and B = first order rate constant obtained from linear regression analysis

RESULTS

The north orchard was sampled more extensively and was the main focus of data analysis. Pre-application levels in the four plots monitored ranged from none detected to 0.09 ug/cm^2 azinphosmethyl (see Table II). Post-application sampling was conducted at three heights in the canopy (4, 7 and 11 feet) at intervals over the next 8 weeks. Azinphosmethyl oxon (range: 0.002-0.011 ug/cm^2) was detected in one-third of the samples and constituted about one to five percent of the thion levels. The residue decay curves for each height are presented in Figures I-III and a composite graph of all three heights is presented in Figure IV. The r^2 values for the decay curves at each height are significant at the $p = 0.01$ level. The decay constants, half-lives and computer-driven initial residues are given in Table III.

Examination of leaf dislodgeable residue levels demonstrate there are differences that are related to height. At t = 0, the lowest zone had 3 times the azinphosmethyl deposition of the highest zone and 2 times the initial deposition of the middle, 7-foot zone. For the first 4 weeks post-application, when all heights were sampled at each time interval, the residues are greatest in the 4-foot zone, intermediate in the 7-foot zone and lowest in the 11-foot zone. In order to receive maximum benefit from a pesticide application, orchard sprayers are generally adjusted to deliver 2-3 times the depostion to the lower half of the tree as compared to the upper half of the tree (8). Thus the trend toward greater residues in the lower portion of the foliage is expected.

The azinphosmethyl decay rates also differ by height, with the relative rate of decay at 4 feet being 1.5 times the rate at 7 feet. The relative rate of decay at 11 feet is 2.2 times as fast as at 7 feet. Though the decay rates differ by height, there is no predictable relationship between height and rate of decay. For example, the 7-foot zone had the median initial residue level, but the slowest decay rate. A comparison of the individual rate constants for each height show the 4- and 7- foot levels and the 7- and 11-foot levels differ (the confidence intervals do not overlap), but there is no difference in decay rates between the 4 and 11 foot levels.

The corresponding half-lives derived from the decay rate constants similarly do not have a predictable relationship to height. The highest zone had the shortest half-life (12 days), the middle zone had the longest half-life (25 days) and the lowest zone was intermediate, with a half-life of 17 days. As with the decay rate constants, the $t_{1/2}$ values of 17 and 25 days differ significantly, as do 12 and 25 days, but 12 and 17 days do not.

After four weeks, sampling was not conducted at all height zones for each sampling interval, due to standing water in the orchard making access impossible. The dislodgeable residues in the 7- and 4-foot zones approached a similar level at 8 weeks post-application (see Table II).

In the south orchard, sampling was insufficient for the purposes of estimating decay rate or residue differences by height. The azinphosmethyl levels ranged from 0.36-0.71 ug/cm^2 at 8 days post-application, and from 0.13-0.28 ug/cm^2 at 14 days post-application (See Table I). At 8 days post-application, the residues appear higher in the 7-foot sampling zone compared to residues in the 4-foot and the 11-foot sampling zones. The residues at 8 and 14 days fall within the ranges found for the north orchard only for the 7-foot height. The residues for the 11-foot zones are higher than those found in the north orchard and those at 4 feet fall below the levels found in the north orchard. No oxon was detected in any of the samples. Sampling was discontinued after 14 days, and no further analysis of the results was conducted.

DISCUSSION

This is the first study undertaken by the Worker Health and Safety Branch (WH&S) to investigate the pattern of dislodgeable foliar residue degradation at specific height intervals in orchard foliage. The results indicate that initial residues are a function of height and that they decline with increasing height. This is expected from the usual spray pattern of the typical orchard pesticide application. Azinphosmethyl decay rates differ by height as well, but are not a function of initial residues. The decay rate for the 11-foot zone is most rapid and is 1.5 to 2.2 times the rate for the other two heights. A faster decay would be expected for the highest zone as this area has sparser foliage and greater penetration of sunlight than the lower zones and photodegradation of the pesticide may take place to a greater extent. The decay rate is slower at 4 and 7 feet, but is independent of initial residues, i.e., the lowest zone, with the greatest initial residue does not have the slowest decay. The relationship between decay rate and height in the lower zones may be obscured by a multiplicity of factors, including the amount of foliage, amount and stage of fruit development, available sunlight, varying humidity at each height, behavior of residues of electrostatically applied material and type of irrigation. No conclusions can be drawn as to the effects of overhead irrigation on azinphosmethyl decay. However, overhead irrigation beginning 12 hours after application does not appear to dislodge azinphosmethyl residues as there is no significant difference ($p < 0.05$) residues at each height between day 1 and day 2.

Results from this study were compared to results from previous azinphosmethyl studies conducted by WH&S. In one study (9), the degradation of azinphosmethyl residues on pear foliage was monitored. Application was at a similar rate (0.75 lb a.i./acre) and also by electrostatic sprayer. The irrigation water was applied by portable ground sprinklers. The foliage was sampled at approximately four to six feet from the ground. No samples were collected past 39 days. The azinphosmethyl residues during the fourth week (27 - 32 days) averaged 0.36 ug/cm^2 (SD 0.18). In the present study, the average azinphosmethyl residue in the same height zone (4 to 7 feet) at four weeks post-application was 0.30 ug/cm^2 (SD 0.13). Although the crop type and irrigation method differ, the azinphosmethyl residues at similar sampling intervals are comparable.

In another study conducted by WH&S (10), the degradation of azinphosmethyl residues on plum foliage was monitored at six sites. The applications were made by airblast sprayers at the rate of 1.5 lb a.i./acre (2.5 times greater than the application rates in this study) and the initial depostion was approximately two times higher. The orchards were flood irrigated. Sampling was conducted at approximately four to six feet from the ground. The average azinphosmethyl half-life for the six fields was 20 days. In the present study, the average azinphosmethyl half-life for the similar height zone (the mean of the 4 and 7 foot levels) heights is 21 days. Despite the many differences between the studies, the azinphosmethyl half-lives are similar.

CONCLUSIONS

The data obtained from the analysis of apple foliage for azinphosmethyl residues were sufficient to characterize initial deposition and decay rates at three heights in the canopy for the north orchard location. Initial deposition is a function of height. Although the decay rates of azinphosmethyl at four, seven and 11 feet were slightly different, the rates did not appear to be related to the height in the canopy or initial deposition. Further studies of this type would be required to investigate other aspects such as crop differences, irrigation type, geographic location or application method.

TABLE I

H. P. METZLER, MADERA: AZINPHOSMETHYL ON APPLES

SOUTH SITE

AZINPHOSMETHYL RESIDUE IN ug/cm^2

PLOT	HEIGHT	8 DAYS	14 DAYS (3.6" WATER)
1	11 FEET	0.35	0.20
	7 FEET	0.65	0.20
	4 FEET	0.36	0.15
2	11 FEET	0.43	0.25
	7 FEET	0.64	0.25
	4 FEET	0.44	0.25
3	11 FEET	0.54	0.21
	7 FEET	0.71	0.28
	4 FEET	0.48	0.13
4	11 FEET	0.40	0.20
	7 FEET	0.61	0.20
	4 FEET	0.57	0.24

Application on May 2, 1988. No azinphosmethyl oxon was detected on any of the samples.

TABLE II

H. P. METZLER, MADERA: AZINPHOSMETHYL, 0.61 #/ACRE, APPLIED TO APPLE FOLIAGE
NORTH SITE

APPLICATION ON 5-18-88
SAMPLES TAKEN AT THREE HEIGHTS IN TREES
AZINPHOSMETHYL (AZM) AND AZM OXON RESIDUES REPORTED IN ug/cm^2

INTERVAL	HEIGHT					
	11 FEET		7 FEET		4 FEET	
	AZM	OXON	AZM	OXON	AZM	OXON
PLOT 1 (Rows 119-120)						
PRE	0.03	ND	0.07	ND	0.09	ND
DAY 1	0.65	ND	0.89	ND	0.97	ND
DAY 2	0.60	ND	0.78	ND	1.02	ND
DAY 5	0.29	ND	0.39	ND	0.59	ND
DAY 8	0.30	0.003	0.60	0.004	0.72	0.006
2 WEEKS	0.20	ND	0.20	ND	0.40	ND
4 WEEKS	0.20	ND	0.33	0.003	0.42	0.004
6 WEEKS	NS	NS	0.23	0.006	NS	NS
7 WEEKS	NS	NS	0.33	0.007	NS	NS
8 WEEKS	NS	NS	0.29	0.011	0.13	0.006
PLOT 2 (Rows 129-130)						
PRE	0.03	ND	0.08	ND	0.09	ND
DAY 1	0.40	ND	1.12	ND	1.19	ND
DAY 2	0.55	ND	1.22	ND	1.47	ND
DAY 5	0.19	ND	0.67	ND	0.91	ND
DAY 8	0.10	ND	0.77	0.004	0.72	0.006
2 WEEKS	0.05	ND	0.55	0.002	0.65	0.005
4 WEEKS	0.15	0.002	0.22	0.003	0.42	0.003
6 WEEKS	NS	NS	0.34	0.006	NS	NS
7 WEEKS	NS	NS	0.34	0.005	NS	NS
8 WEEKS	NS	NS	0.17	0.007	0.16	0.006
PLOT 3 (Rows 139-140)						
PRE	NS	NS	NS	NS	0.06	ND
DAY 1	0.41	ND	1.05	ND	1.15	ND
DAY 2	0.58	ND	1.20	ND	1.33	ND
DAY 5	0.22	ND	0.61	ND	1.10	ND
DAY 8	0.12	ND	0.59	ND	0.80	0.003
2 WEEKS	0.12	ND	0.48	ND	0.77	0.003
4 WEEKS	0.01	ND	0.25	ND	0.47	0.003
6 WEEKS	NS	NS	0.30	0.009	NS	NS
7 WEEKS	NS	NS	0.18	ND	NS	NS
8 WEEKS	NS	NS	0.19	0.009	0.17	0.005

ND: none detected, below 0.003 ug/cm^2
NS: no sample taken

TABLE II, cont.

INTERVAL	HEIGHT					
	11 FEET		7 FEET		4 FEET	
	AZM	OXON	AZM	OXON	AZM	OXON
PLOT 4 (Rows 149-150)						
PRE	NS	NS	NS	NS	0.01	ND
DAY 1	0.42	ND	1.03	ND	1.67	ND
DAY 2	0.53	ND	1.11	ND	1.51	ND
DAY 5	0.22	ND	0.67	ND	0.86	ND
DAY 8	0.09	ND	0.09	0.002	0.76	0.002
2 WEEKS	0.11	ND	0.38	ND	0.70	0.007
4 WEEKS	0.04	ND	0.09	ND	0.20	0.002
6 WEEKS	NS	NS	0.26	0.007	NS	NS
7 WEEKS	NS	NS	0.10	ND	NS	NS
8 WEEKS	NS	NS	0.06	0.004	0.06	0.004

ND: none detected, below 0.002 ug/cm^2
NS: no sample taken

TABLE III
DECAY RATES AND INITIAL RESIDUES OF AZINPHOSMETHYL ON APPLES AT THREE HEIGHTS

HEIGHT FEET	DECAY CONSTANT AND SD $(ug/cm^2)/day$	HALF-LIFE days	INITIAL RESIDUE ug/cm^2
4	-0.018, 0.001	17	1.19
7	-0.012, 0.002	25	0.77
11	-0.026, 0.009	12	0.39

Fig. 1 Azinphosmethyl Decay on Apples

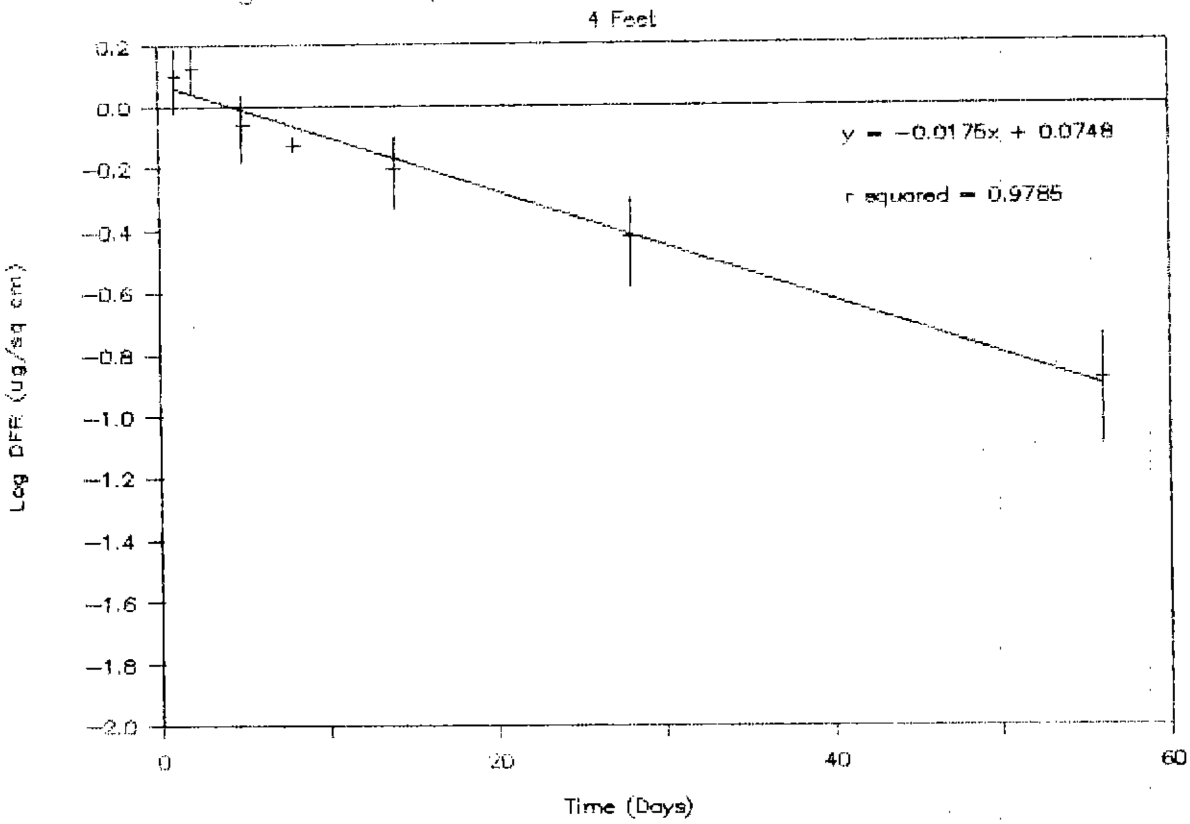


Fig. 2 Azinphosmethyl Decay on Apples

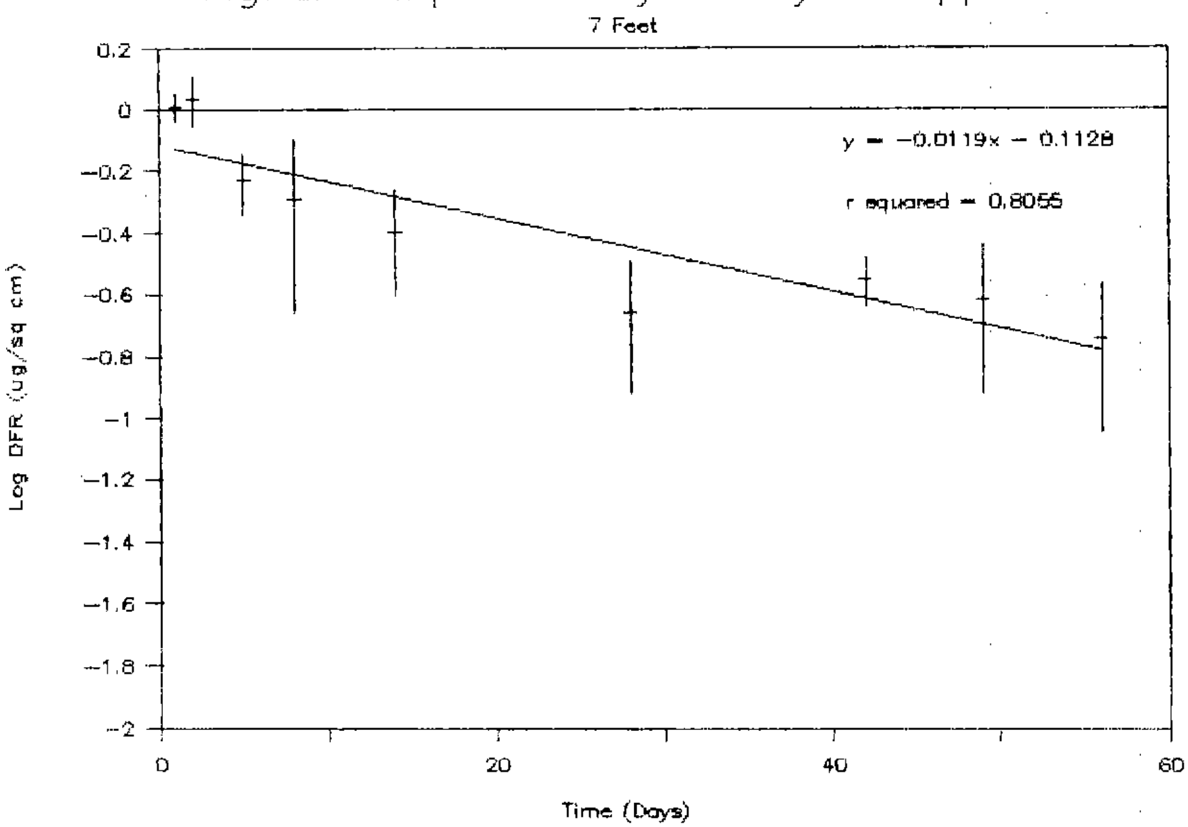


Fig. 3 Azinphosmethyl Decay on Apples

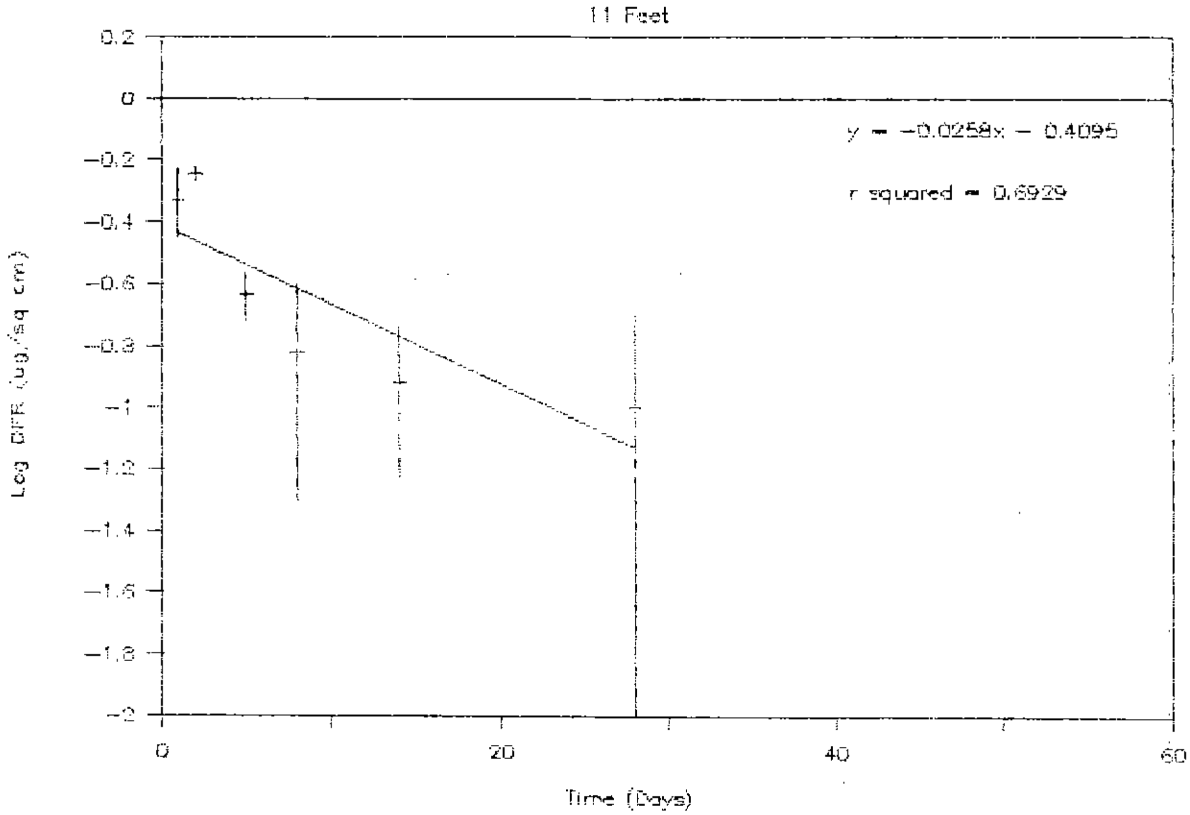
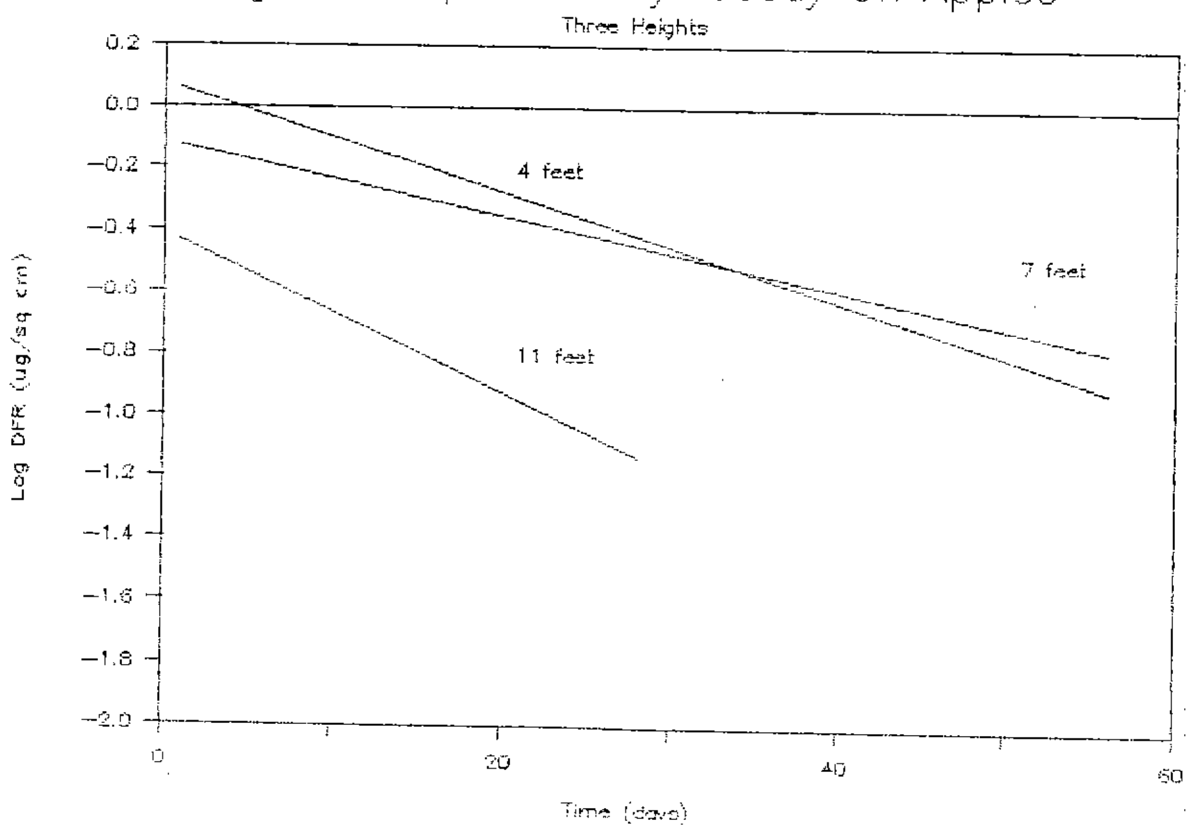


Fig. 4 Azinphosmethyl Decay on Apples



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